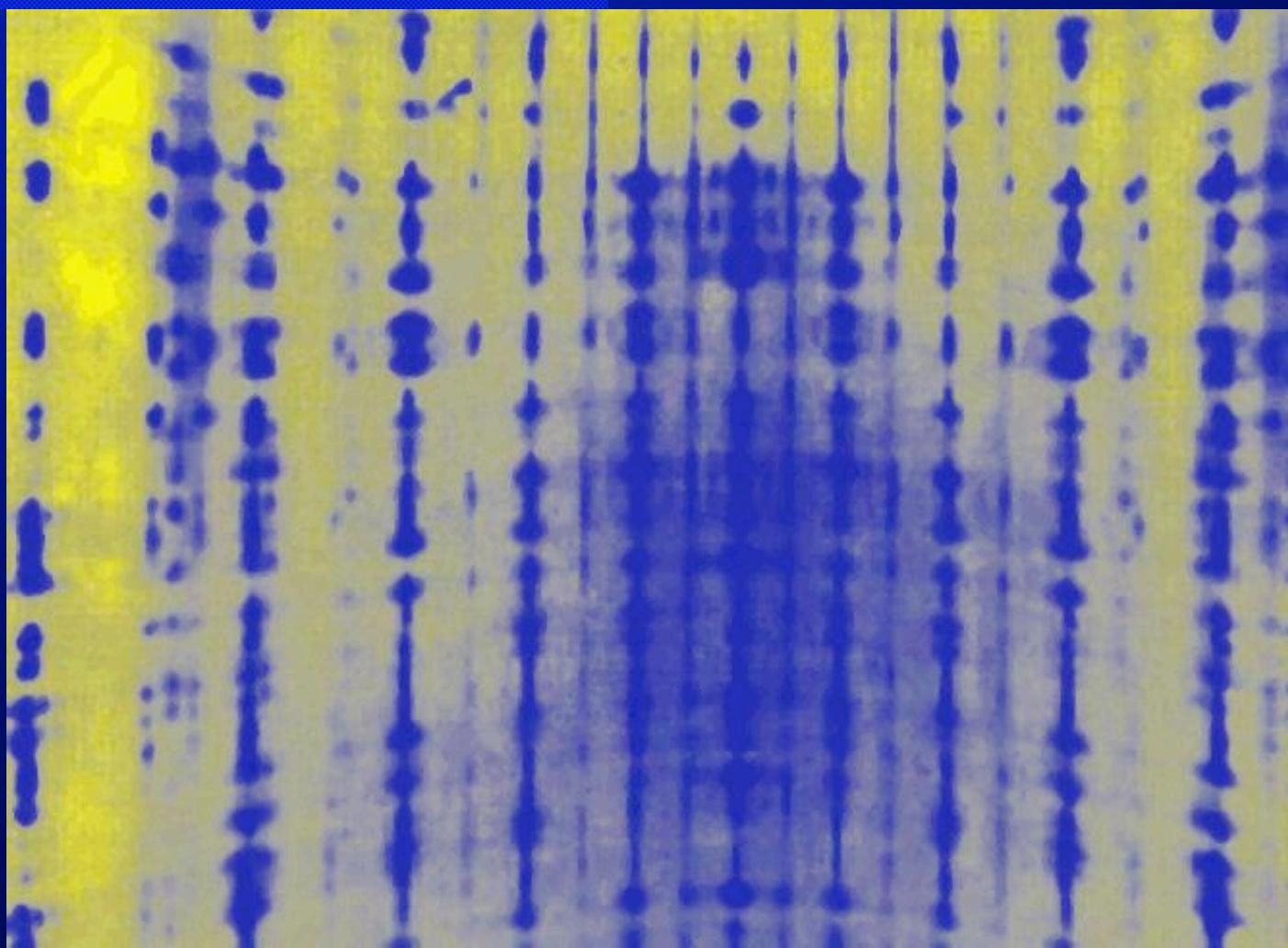




Diffuse Neutron and X-ray Scattering: Introduction and Scientific Value of Comparative Studies

Friedrich Frey
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Crystallography
LMU München

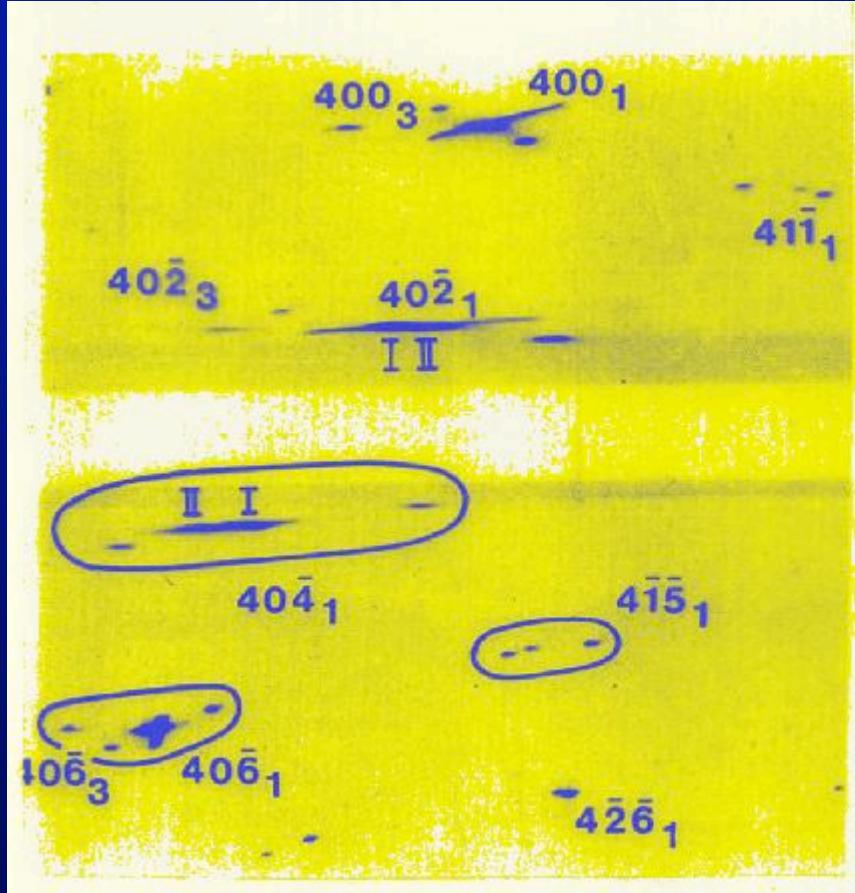
Examples



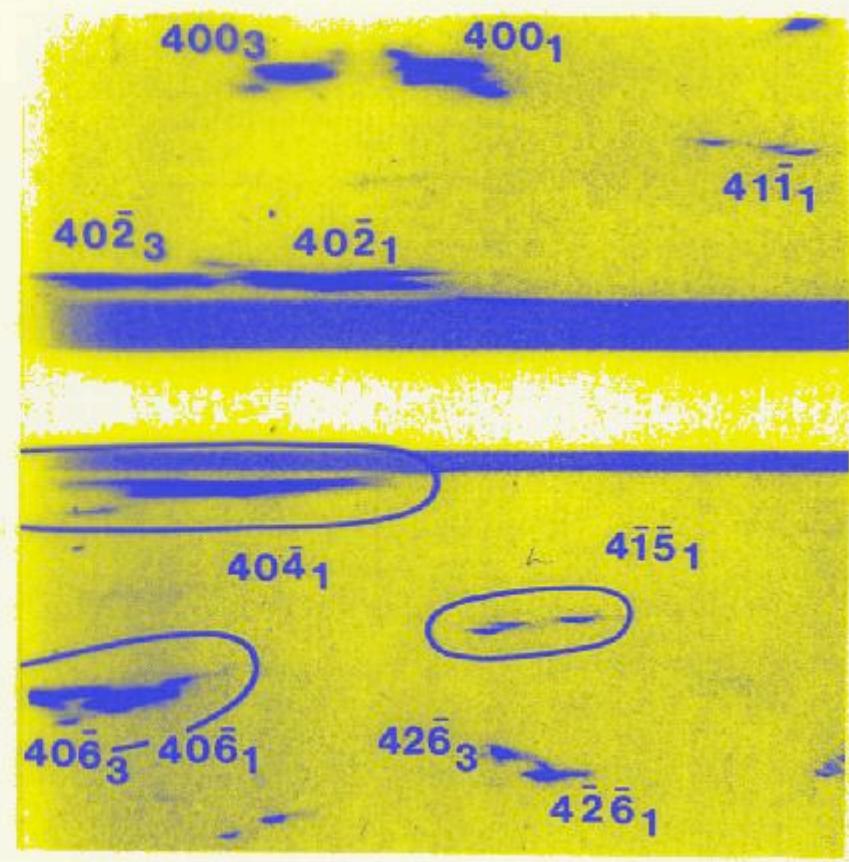
Urea/HD
32 K

Examples

Jagodzinski and Korekawa, 1973



terrestrial feldspar



lunar feldspar

Outline

Disorder – Diffuse Scattering

X-Rays vs. neutrons

General aspects

Experimental aspects

Examples

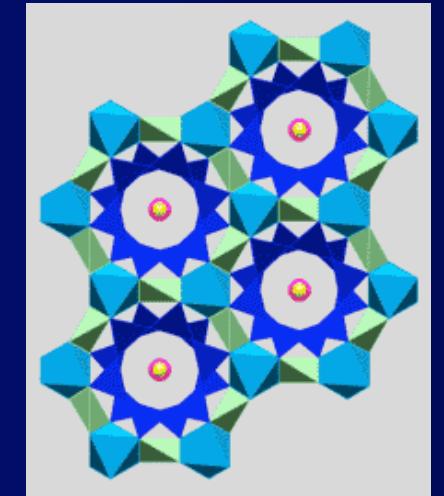
Zirconia

Decagonal quasicrystals

Dedicated Neutron Instrument:RESI at the FRMII Reactor



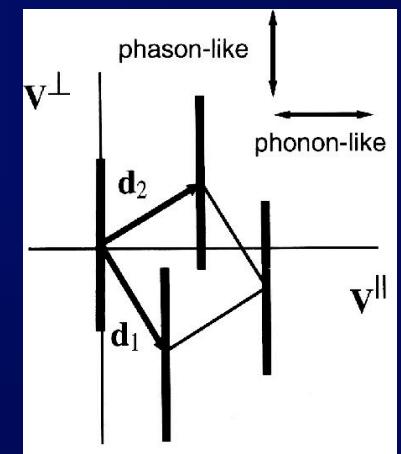
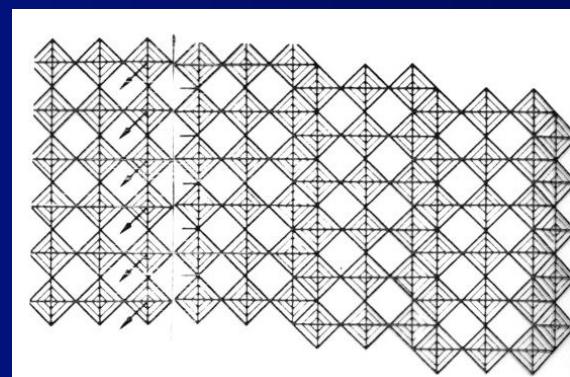
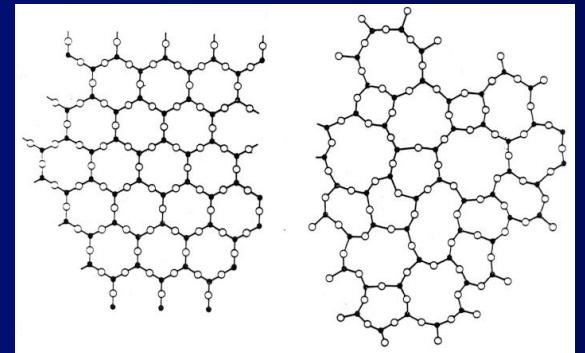
Structure



- Long range order of atoms in a lattice
(1D...3D...6D)
- periodic (crystalline) – aperiodic (quasicrystalline)
- deviations □ disorder, defects
 - short-range order
 - re-ordering, transformations, ... as a function of external fields
 - dynamics - kinetics (time dependence)

Structural fluctuations: „disorder“

- displacive/positional
- chemical/substitutional
- domain-like {
 - twin
 - chemical
 - out-of-phase
 - layer-stacking
- modulated/superstructure
- orientational \square liquid crystals
- \square phasonic \square quasicrystal



Scattering I

General

Amplitude of a scattered wave:

$$A(\mathbf{Q}) = \langle \psi(\mathbf{x}) \exp(i\mathbf{Q}\cdot\mathbf{x}) \rangle d\mathbf{x}$$

Intensity:

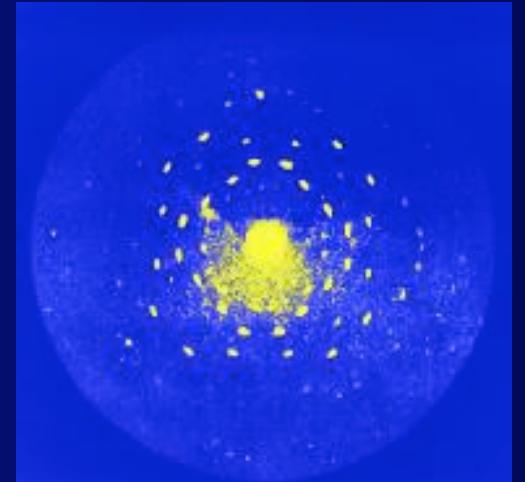
$$I = A(\mathbf{Q})A^*(\mathbf{Q}) = \langle \psi(\mathbf{x})\psi^*(-\mathbf{x}) \rangle$$

If an average structure exists:

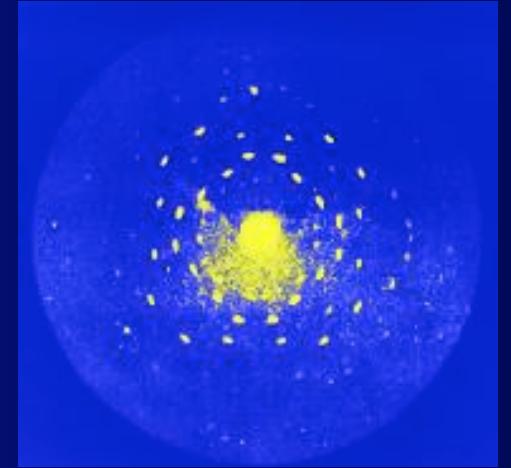
$$\langle \psi(\mathbf{x}) \rangle = \langle \psi(\mathbf{x}, t) \rangle_{x,t} + \langle \delta\psi(\mathbf{x}, t) \rangle \quad (\langle \delta\psi \rangle = 0)$$

average fluctuations (static, dynamic)

$$F.T.\{\psi\} \equiv F(\mathbf{Q}, \psi) = F.T.\{\langle \psi \rangle\} + F.T.\{\delta\psi\} \equiv \langle F(\mathbf{Q}) \rangle + \langle \delta F(\mathbf{Q}) \rangle$$



Scattering II



Average structure (periodic or aperiodic)

$$\langle \square \rangle = \langle \square_c \rangle \square I; \quad \langle \square_c \rangle = 1/N \square_i \square_i; \quad I = \text{lattice in } n\text{-D-direct space} \quad ^n$$

$$\langle A \rangle = \langle F \rangle \cdot L = \square_i \langle F \rangle \exp(iQr_i); \quad L = \text{lattice in } n\text{-D-reciprocal space} \quad ^{*n}$$

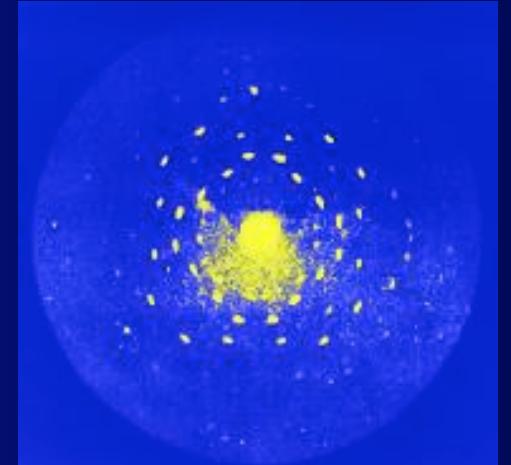
(\square denotes convolution product)

Patterson function (autocorrelation function)

$$\begin{aligned} \langle \square(x) \square(-x) \rangle &= \langle (\langle \square \rangle + \square \square) \square (\langle \square \rangle + \square \square) \rangle \\ &= \langle \square \rangle \square \langle \square \rangle + \langle \square \square \rangle \square \langle \square \square \rangle \end{aligned}$$

$$\begin{aligned} F.T.(\langle \square(x) \square(-x) \rangle) &= \langle A \rangle \langle A^* \rangle + \langle \square A \square A^* \rangle \\ &= | \langle F \rangle |^2 L + \langle \square_i \square_j \square F_i \square F_j^* \exp(iQ(r_i - r_j)) \rangle \\ &= I_{\text{Bragg}} + I_{\text{diffuse}} \end{aligned}$$

Scattering III: Diffuse scattering



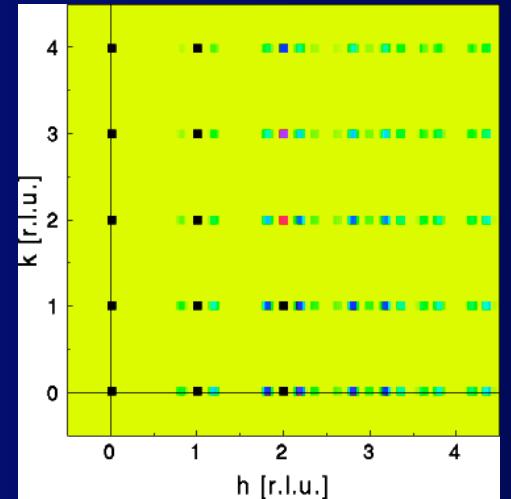
$$\langle A \rangle = A - \langle A \rangle = \sum_i (F_i - \langle F \rangle) \exp(iQr_i)$$
$$= \sum_i (\langle F_i \rangle \exp(iQr_i))$$

$$I_D = \sum_k \langle \sum_i F_i F_{i+k}^* \rangle_i \exp\{iQ(r_k)\}$$

$$\text{with } F = f \exp(iQ(r + r))$$

f substitutional (replacement) disorder
 r displacement disorder

longitudinal wave, $q=0.19$



Example 1: Displacive disorder

$\langle \mathbf{r}_i \rangle$ (small): $\exp(i\mathbf{Q}\langle \mathbf{r}_i \rangle) \approx (1 + i\mathbf{Q}\langle \mathbf{r}_i \rangle + \dots)$

$$I_D = Nf^2 \sum_k \sum_i (\mathbf{Q} \langle \mathbf{r}_i \rangle) (\mathbf{Q} \langle \mathbf{r}_{i+k} \rangle) \exp\{i\mathbf{Q}(\mathbf{r}_k)\}$$

□ thermal random vibrations

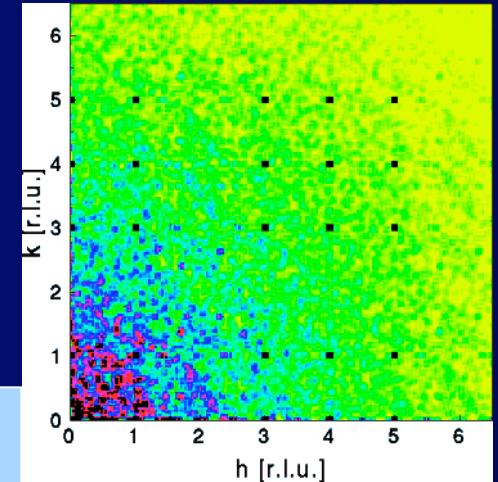
$$I_D = Nf^2 Q^2 \langle \langle \mathbf{r}_i^2 \rangle \rangle_i [= 1 - \exp\{-2W\}]$$

□ periodic modulation: $\langle \mathbf{r}_n \rangle = R_0 \cos(\mathbf{q} \cdot \mathbf{r}_n)$

$$I_D = (Q\langle \rangle)^2 \sum_H \sum_{\mathbf{Q}-\mathbf{H} \pm m\mathbf{q}}$$

(i.e. satellite scattering at positions $m \cdot \mathbf{q}$, $m = \pm 1 \pm 2, \dots$)

occupational disorder
50% of atoms replaced

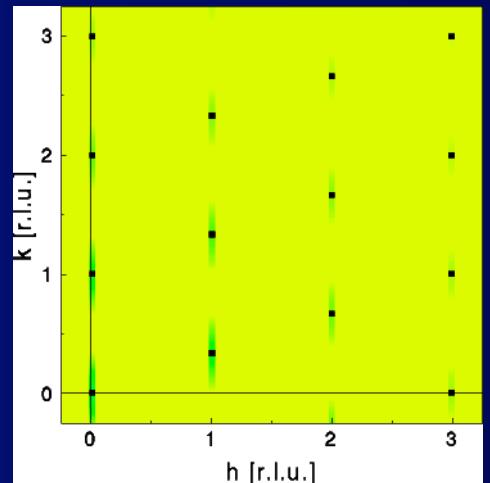


Example 2: substitutional disorder

$c_{i,j}$ = concentrations of species i,j

$p_{i,j}^n$ = conditional probability to find species j at distance n from a site occ. by species i , n = lattice vector

- random: $I_D = N \langle |F|^2 \rangle = N_c \sum_i \sum_j c_i c_j f_i f_j^* [p_{ij}^0/c_j - 1]$
- random, binary: $I_D = N_c c_A c_B (f_A - f_B)^2$ (Laue monotonic scatt.)
- short range correlated: $I_D (I_{sro}) \sim \sum_n \sum_i \sum_j c_i c_j f_i f_j \sum_{ij}^n \cos(\mathbf{Q} \cdot \mathbf{n})$ with: $\sum_{ij}^n = 1 - (p_{ij}^n/c_j)$ (Warren-Cowley sro-parameter)
- periodic modulation: $f_n = f_o \cos(\mathbf{q} \cdot \mathbf{r}_n)$
 $I_D \sim f_o^2 \sum_H I(Q-H \pm \mathbf{q})$ (satellite pair)



Example 3: Domains (two types)

coherent lattices, two different structures F_1, F_2 ,
random distribution of F_1, F_2 with – on the average –
same probabilities. Box function $b(x)$:



Diffraction $B(\mathbf{H}) = F.T. \text{ of } b(\mathbf{x})$:
 $\sim Z(\mathbf{H}) |\langle F(\mathbf{H}) \rangle|^2 + |Z(\mathbf{H}) \square F(\mathbf{H}) \square B(\mathbf{H})|^2$
 $\langle F(\mathbf{H}) \rangle = \underline{\underline{F}}_1 + \underline{\underline{F}}_2; \square F(\mathbf{H}) = \underline{\underline{F}}_1 - \underline{\underline{F}}_2$

Features:

- sharp and diffuse peaks at any lattice point
- sharp peaks governed by $\langle F(\mathbf{H}) \rangle$, diffuse by $\square F(\mathbf{H})$
- diffuseness due to convolution product $Z(\mathbf{H}) \square B(\mathbf{H})$

Disorder of the second kind: loss of LRO

no average structure: lattice replaced by distributions

1D example

$d(z)$ distribution function of first neighbour

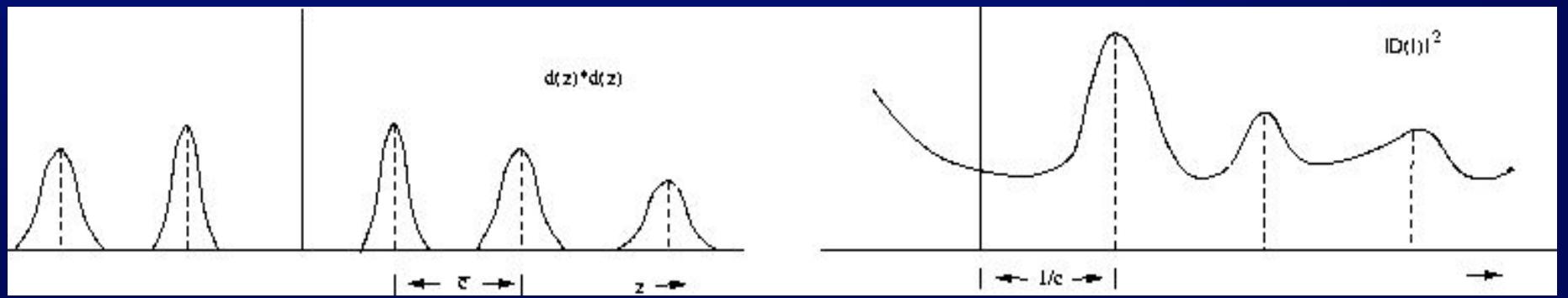
mean distance $\langle c \rangle = \int z d(z) dz$

m^{th} neighbour: $d(z) \int d(z) \int d(z) \dots \int d(z)$

diffuse intensity: $I(l) \sim I F_{\text{mol}} l^2 |D(l)|^2$

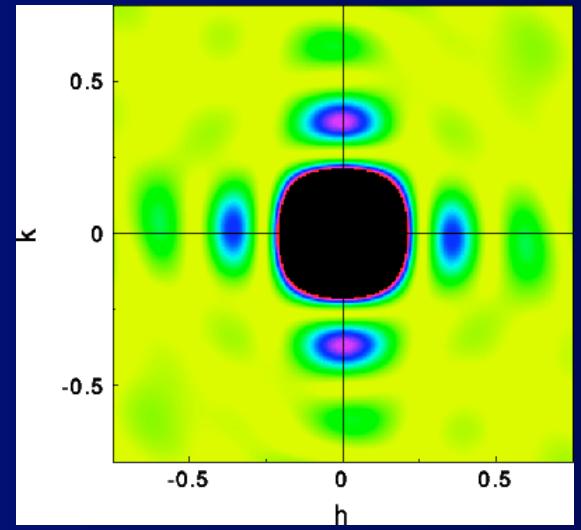
model: $d(z) = 1/\sigma^2 \exp\{-z^2/\sigma^2\}$ (gaussian)

m^{th} diffuse peak: height $\sim |D(m)|^2 \sim 1/m^2$; width $\sim m^2$



Summary - Diffraction

FT of square box
filled with 800 atoms



- modified Bragg reflections
(position, intensity, shape)
 - average crystal structure, i.e. single atom sites
(coord., occ., mean square displacements)
- additional „reflections“ (satellites, sro-peaks)
 - superorder, domains, limited correlation lengths (sro)
 - diffuse scattering extended in (3D or nD) reciprocal space
 - provides information on behaviour of pairs of atoms
 - “about distribution functions

X-rays vs. neutrons 0.5 – 2.5 Å

I. General aspects

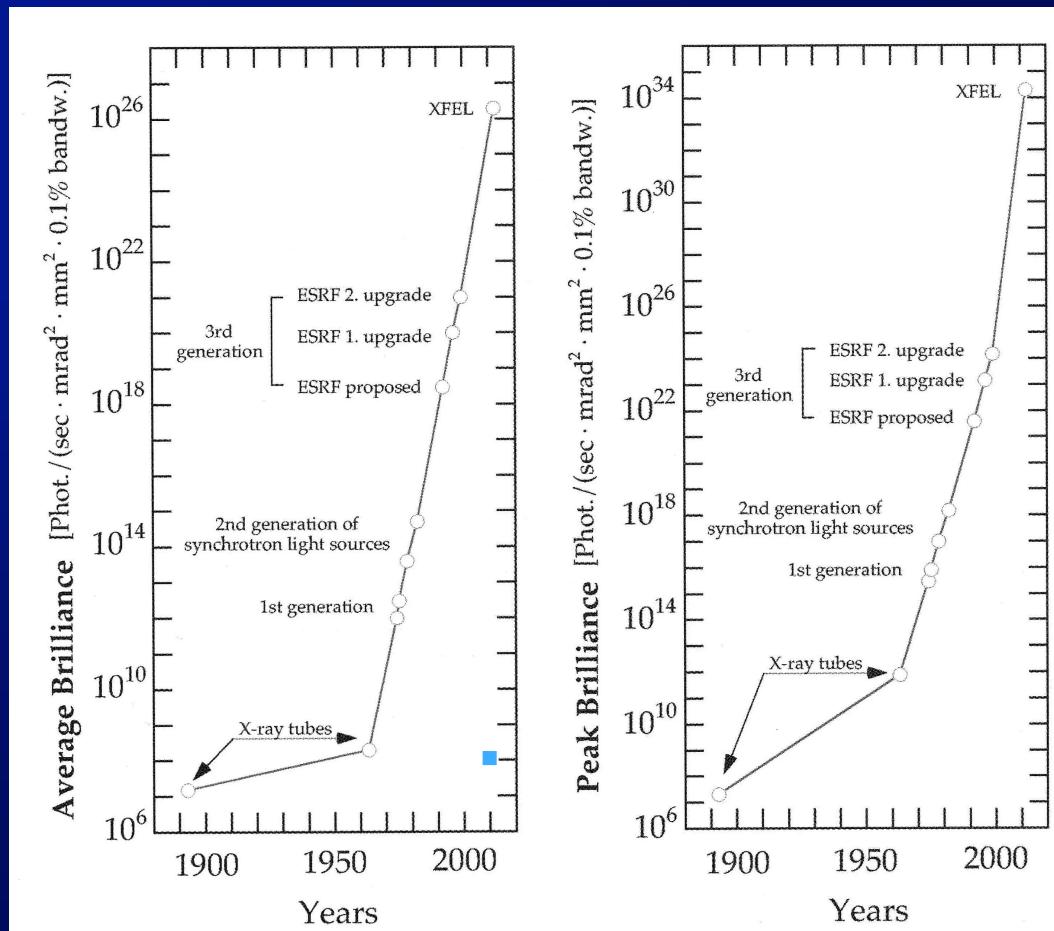
	X-rays	neutrons
absorption	high □ small samples	low □ sample environment
elastic scattering	electronic cloud form factor □ Int. decreases at high Q dependent on Z^2	nuclear no form factor □ high Q irregular variation
background	fluorescence, TDS	incoherent, inelastic (separable by analyser)
contrasting of □f	anomalous scattering use of both x-rays and neutrons	isotope replacement
radiation damage	high (soft matter)	low

II. Practical/experimental aspects

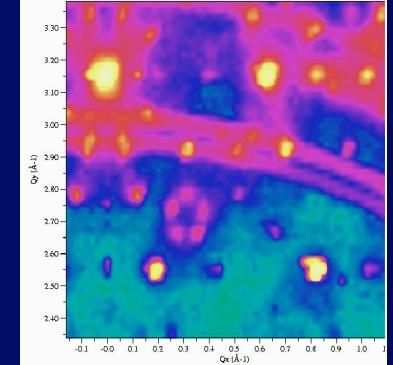
1. Diffuse intensities are (in most cases) weak

- strong x-ray (synchrotron)/neutron sources focussing beam geometries
- low background (sophisticated shielding, neutron guides)

Brilliance of synchrotron sources



■ current reactor sources



II. Practical/experimental aspects

2. Distribution of diffuse intensities in reciprocal space

anisotropically extended, smoothly varying

- relaxed Q-resolution □ neutrons
- resolution, scanning, focussing
- area detectors: IP's, CCD, N-IP (low □background)
- close to/beneath Bragg reflections, satellite scattering
- high angular resolution □ highly collimated synchrotron beams
- energy/time resolution □ TOF diffractometry

II. Practical/experimental aspects

3. Diffuse intensity obscured by non-monochromatic radiation

- high wavelength- (\mathbf{Q} -) resolution □ synchrotron

4. Displacement disorder $\square \mathbf{r}$

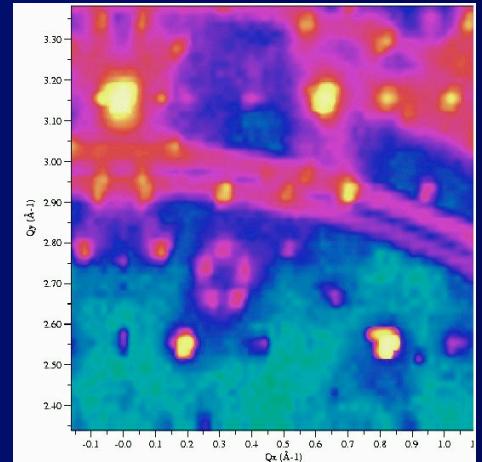
- details may only be seen at high \mathbf{Q} □ neutrons

5. Inhomogeneous disorder: types and degrees in one sample

- scanning micro -diffraction: SXD (micro-focussed x-rays)

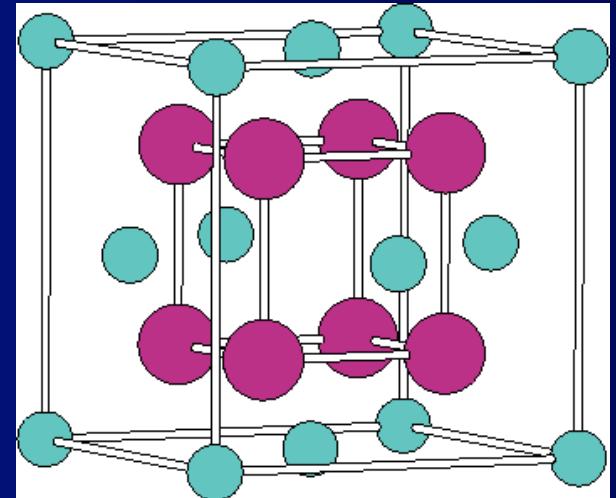
6. Disorder: phase fluctuations □ „speckle“ patterns

(XPCS, X-Ray Photon Correlation Spectroscopy)



Zirconia

$\text{ZrO}_2 \left\{ \begin{array}{l} \text{M}^{2+} \text{O: M=Ca, Mg,...} \\ \text{M}_2^{3+}\text{O}_3: \text{M=Y, Yb, Sc} \\ \text{and/or: exchange O}^{2-} \text{ by N}^{3-} \end{array} \right.$



Fluorite

● Zr (Y)
● O (N, vacancies)

CSZ, YSZ, ...	(Ca, Y,... Stabilized Zirconia)
PSZ	(Partially Stabilized Zirconia)
TZP	(Tetragonal Zirconia Polycrystal)
SCZ	(Scandia Doped Zirconia)

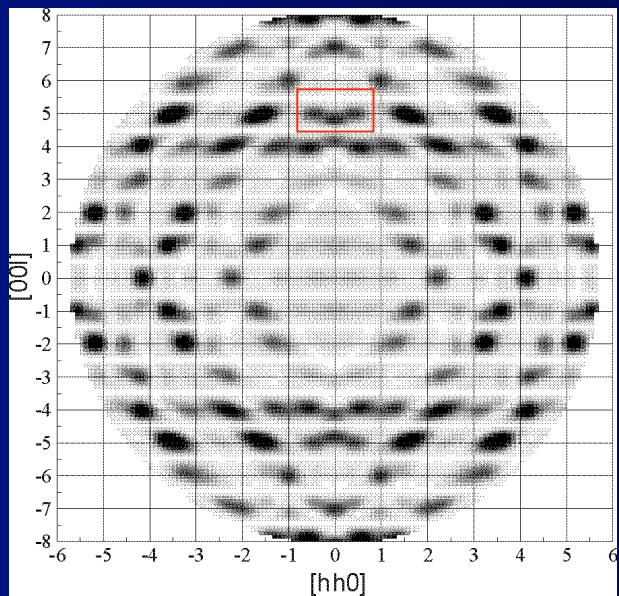
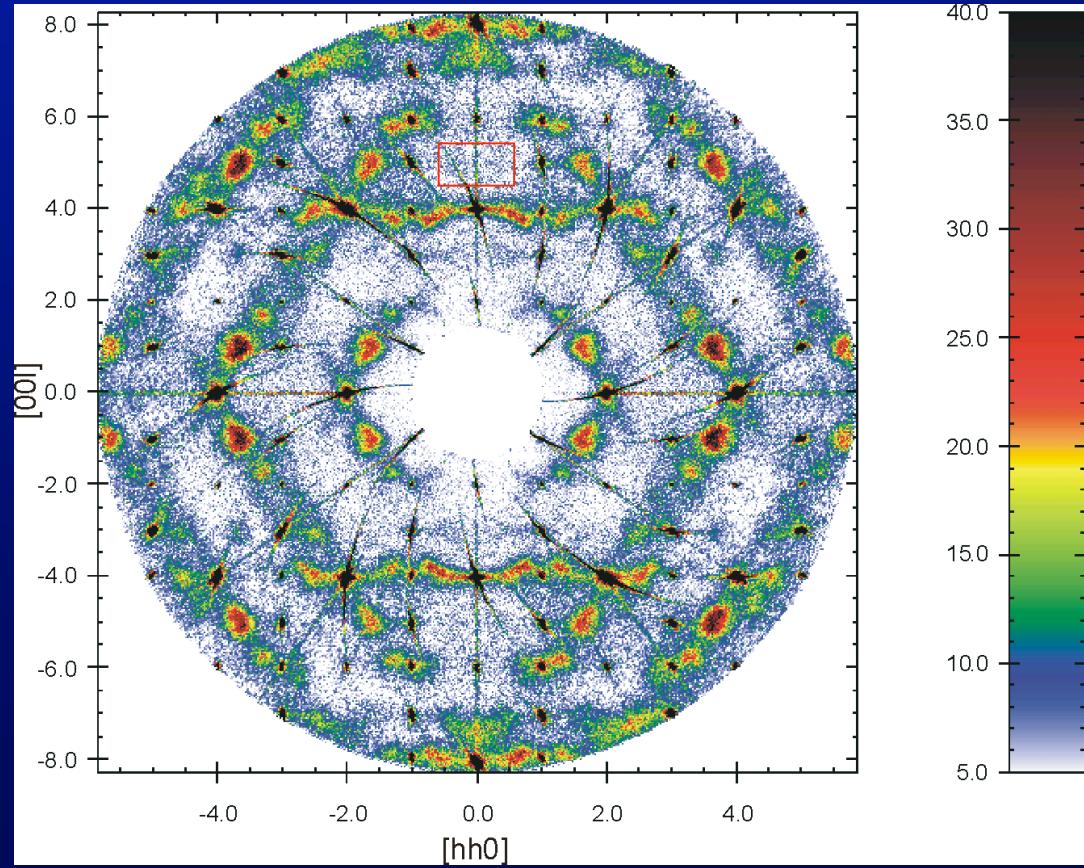
cubic
cub.+tet.+mon.
tet.+cub.
,cub'[] rhomb.

O vacancies [] ionic conductivity [] sensor, fuel cell, ...
higher concentrations [] short range order [] long range order
[] optimum conductivity at ~ 10 mol%

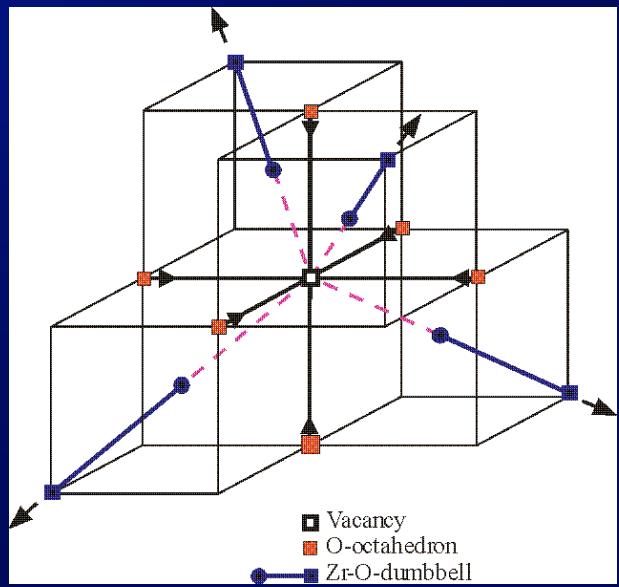
$Zr_{0.96}Y_{0.04}O_{1.64}N_{0.223}$ single crystal

Calculation: 2 clusters along [001]

Experiment: E2/HMI; 0th layer of [1-10] zone

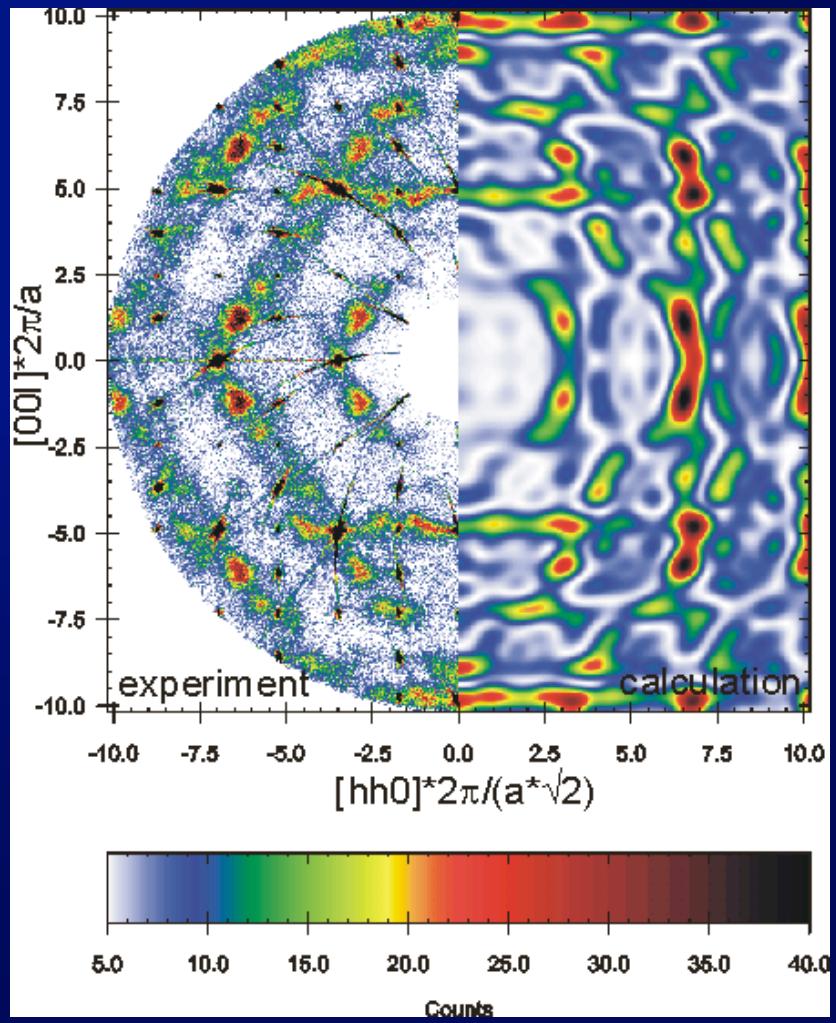
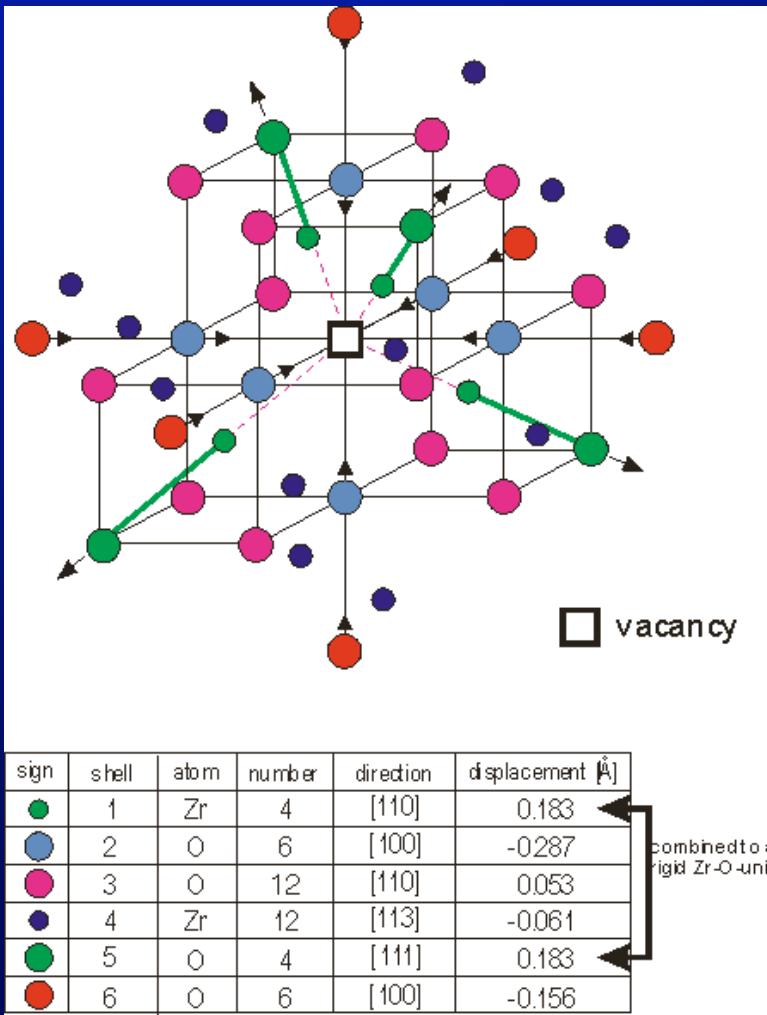


Model cluster



Refinement of model cluster

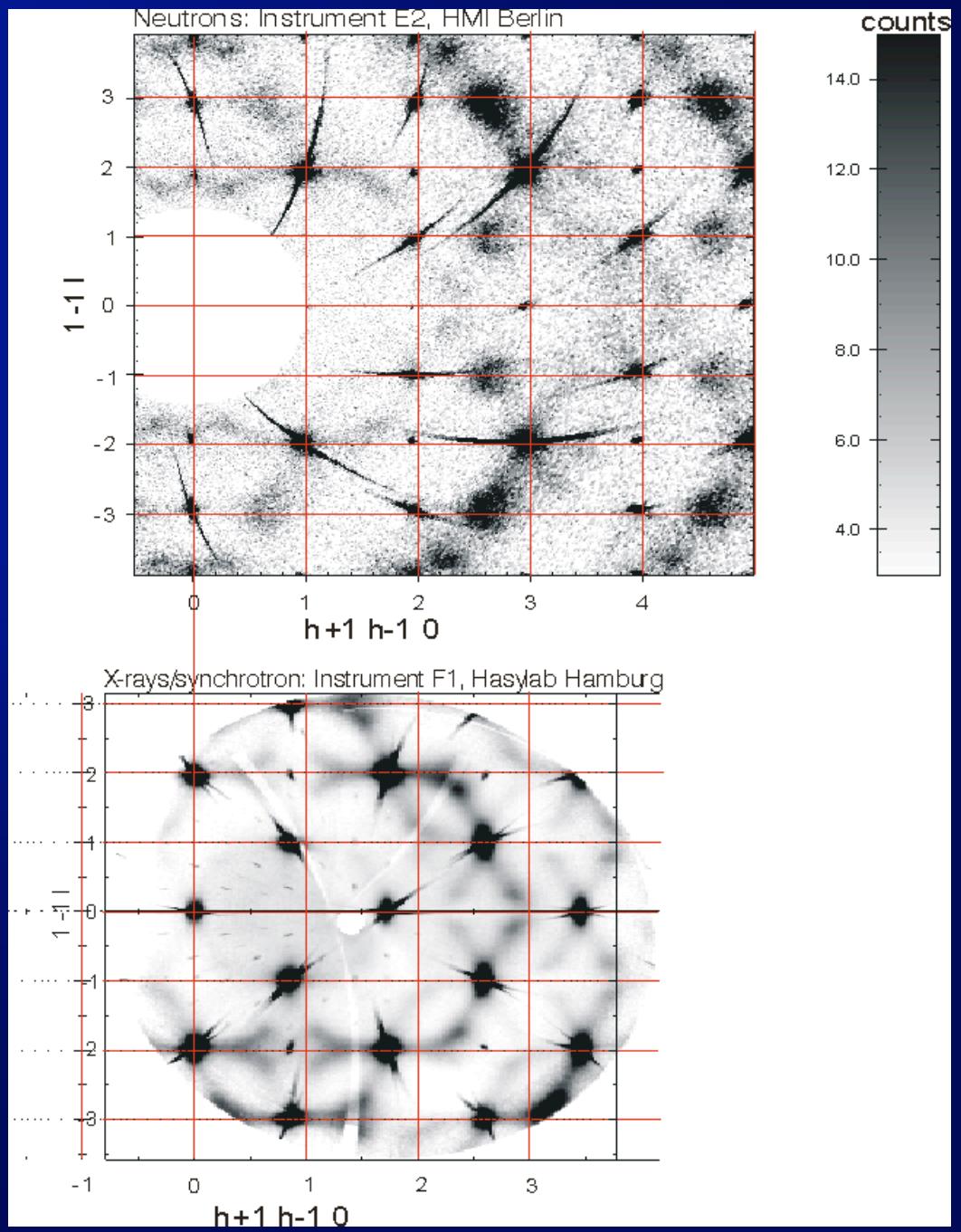
no correlations



Comparison x-ray/neutron

$Zr_{0.96}Y_{0.04}O_{1.64}N_{0.223}$

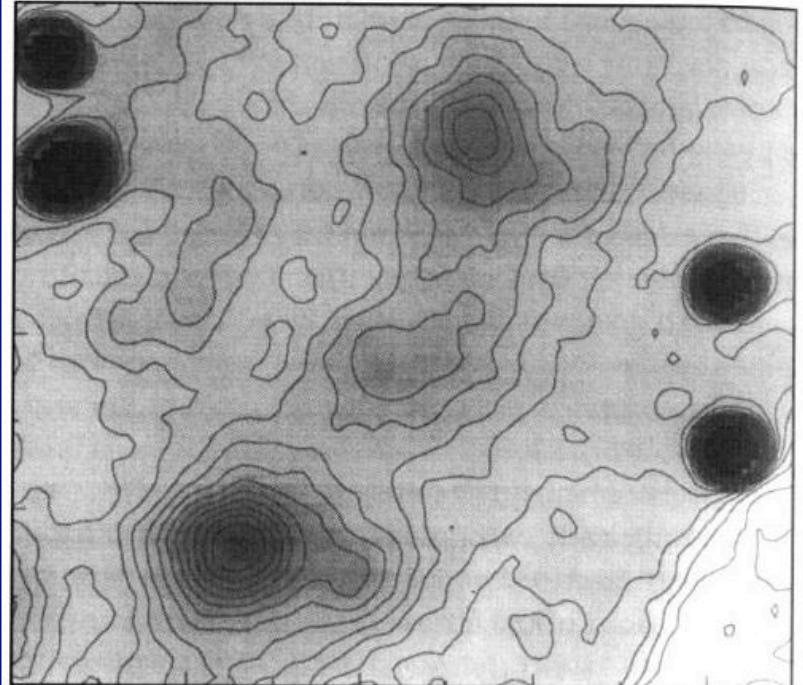
- neutrons: Q-range larger
- characteristic structures of diffuse scattering are similar
- small differences caused by O



Anomalous scattering

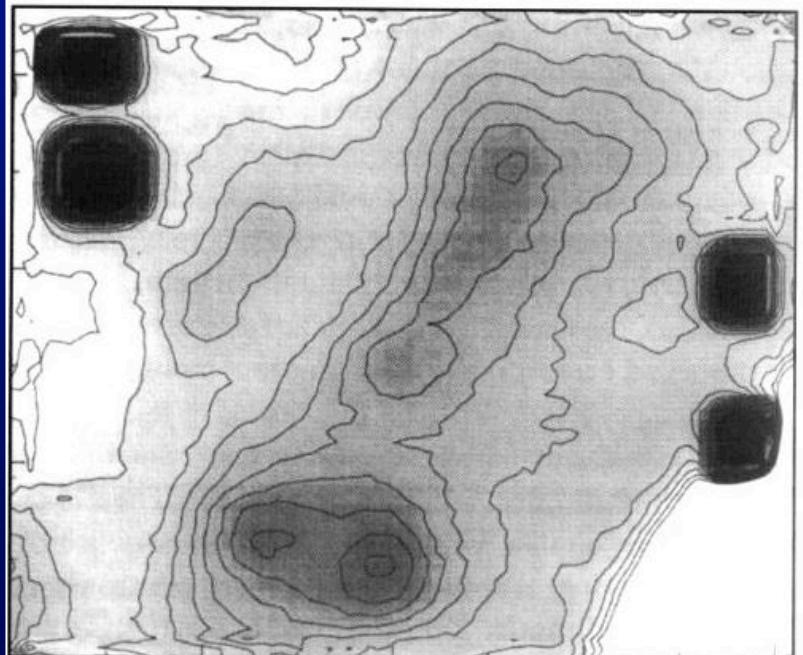
CSZ15 – ZrK edge
DESY/F1, image plate

$$\square = 0.699 \text{ \AA}$$



arbitrary scale

$$\square = 0.679 \text{ \AA}$$

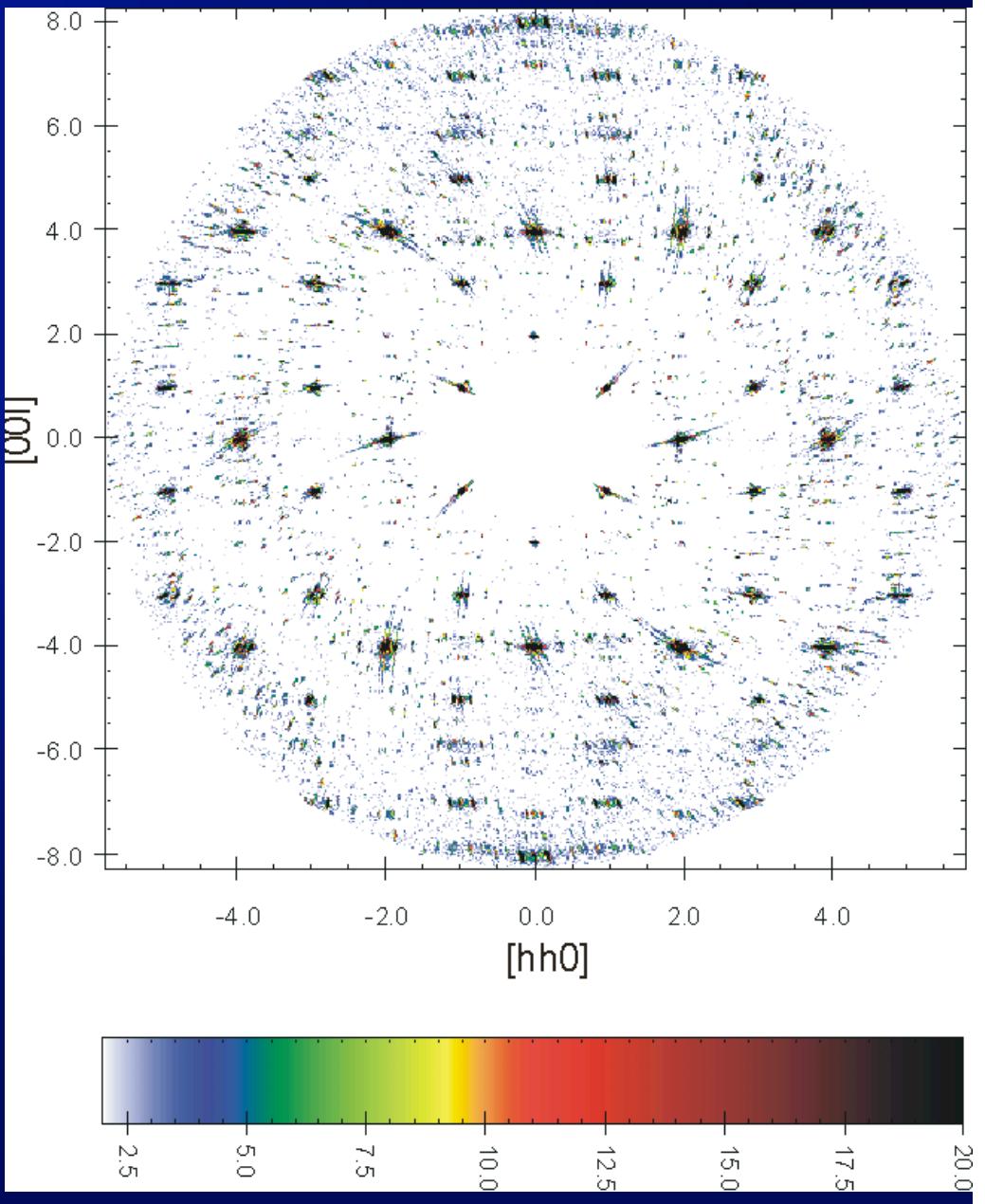


Superstructure reflections

Sc doped Zirconia
(90 mole% ZrO_2 ,
10 mole% Sc_2O_3)

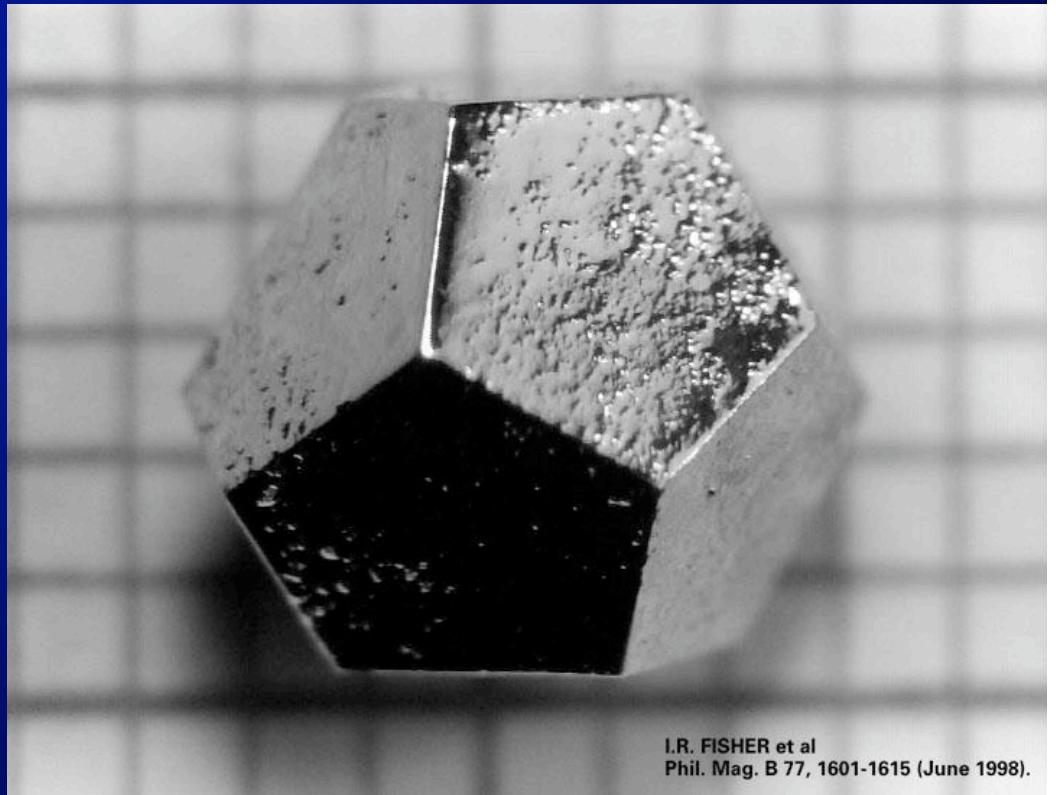
rhombohedral + cubic

E2, HMI Berlin
 $\lambda=0.91\text{\AA}$



Quasicrystallography

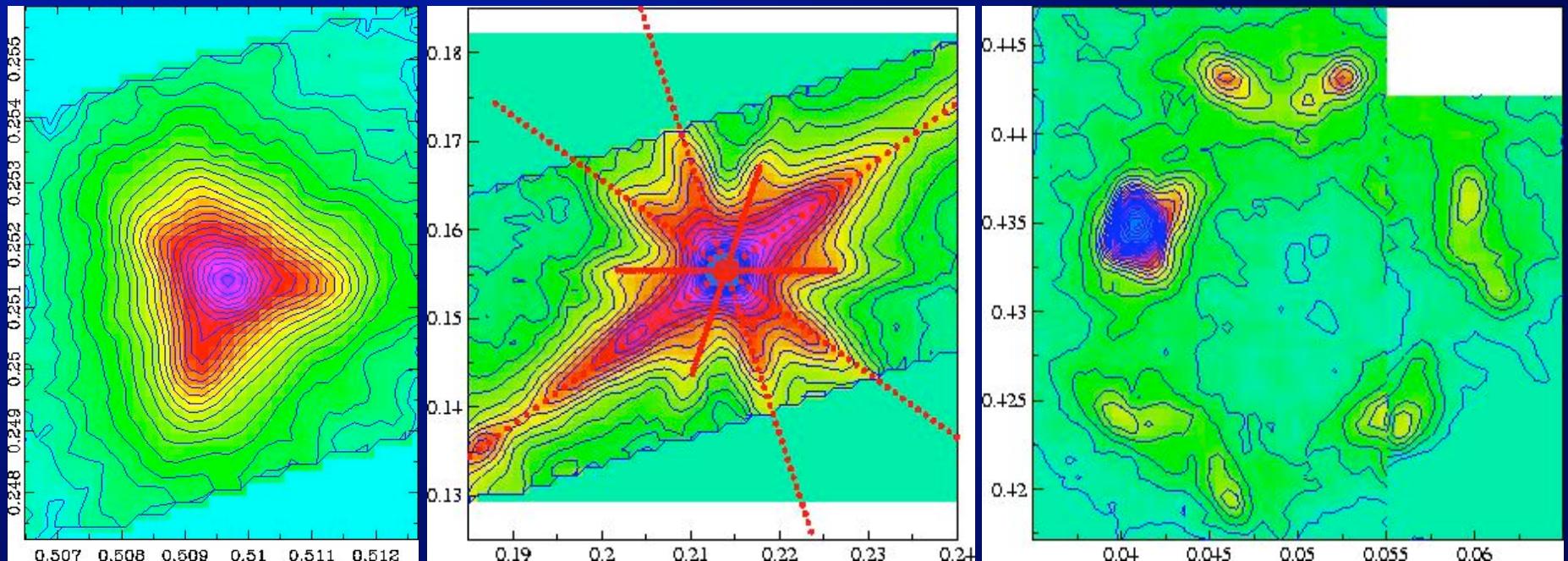
- aperiodic order
- \square -scaling symmetry □
self-similarity
- non-crystallographic
symmetry
(5-, 10-, 12-fold)
- local isomorphism
- icosahedral, decagonal
phases



I.R. FISHER et al
Phil. Mag. B 77, 1601-1615 (June 1998).

Single grain of icosahedral Ho-Mg-Zn

Decagonal phase: typical diffuse phenomena in the quasiperiodic plane



diffuse scattering
near Bragg
reflections

$\text{Al}_{70}\text{Co}_{15}\text{Ni}_{15}$

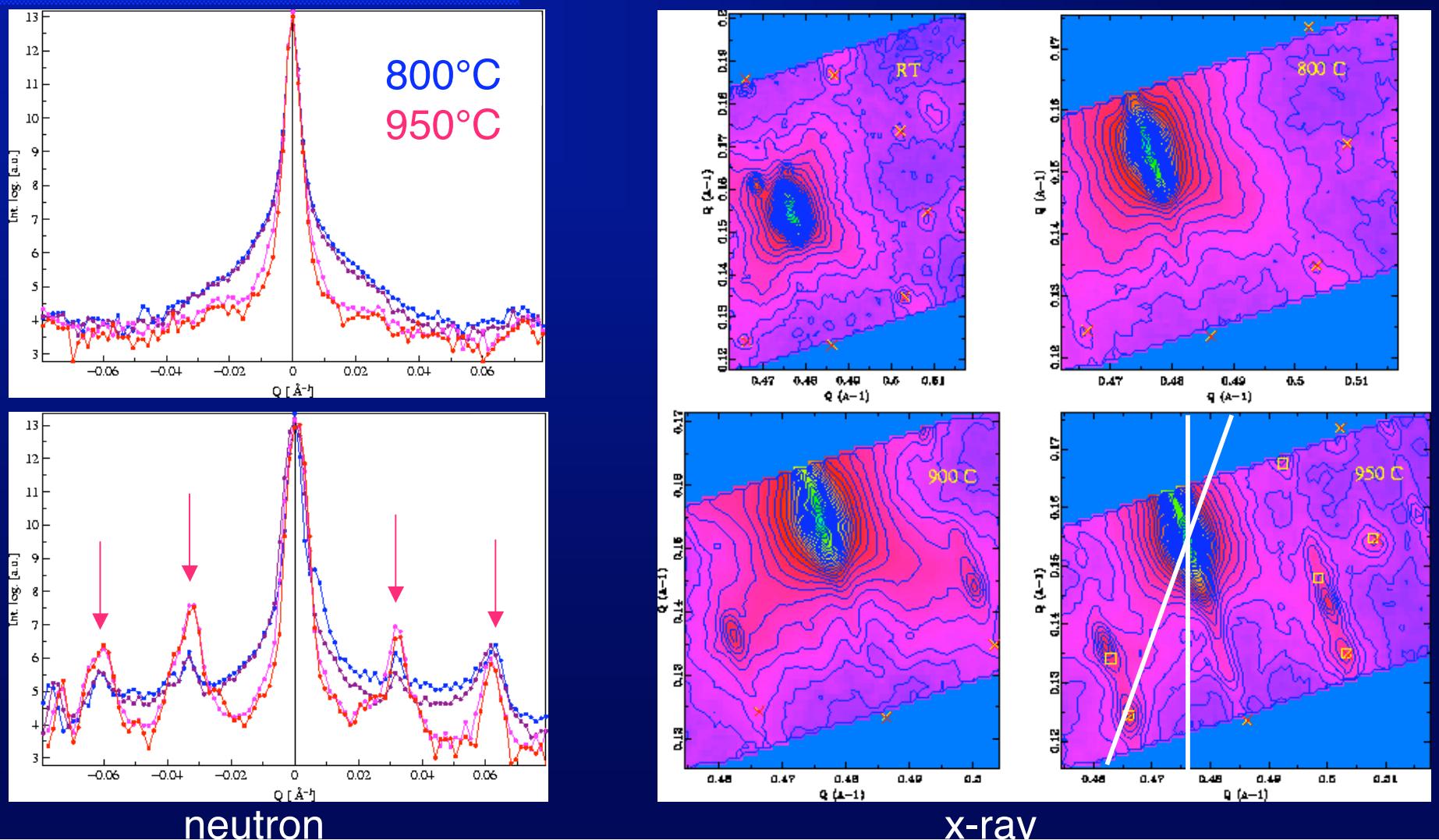
diffuse streaks

$\text{Al}_{62}\text{Cu}_{20}\text{Co}_{15}\text{Si}_3$

sro maxima

$\text{Al}_{72}\text{Co}_{16}\text{Ni}_{12}$

Temperature dependence of diffuse scattering: neutron vs. x-ray



Neutron TOF measurement

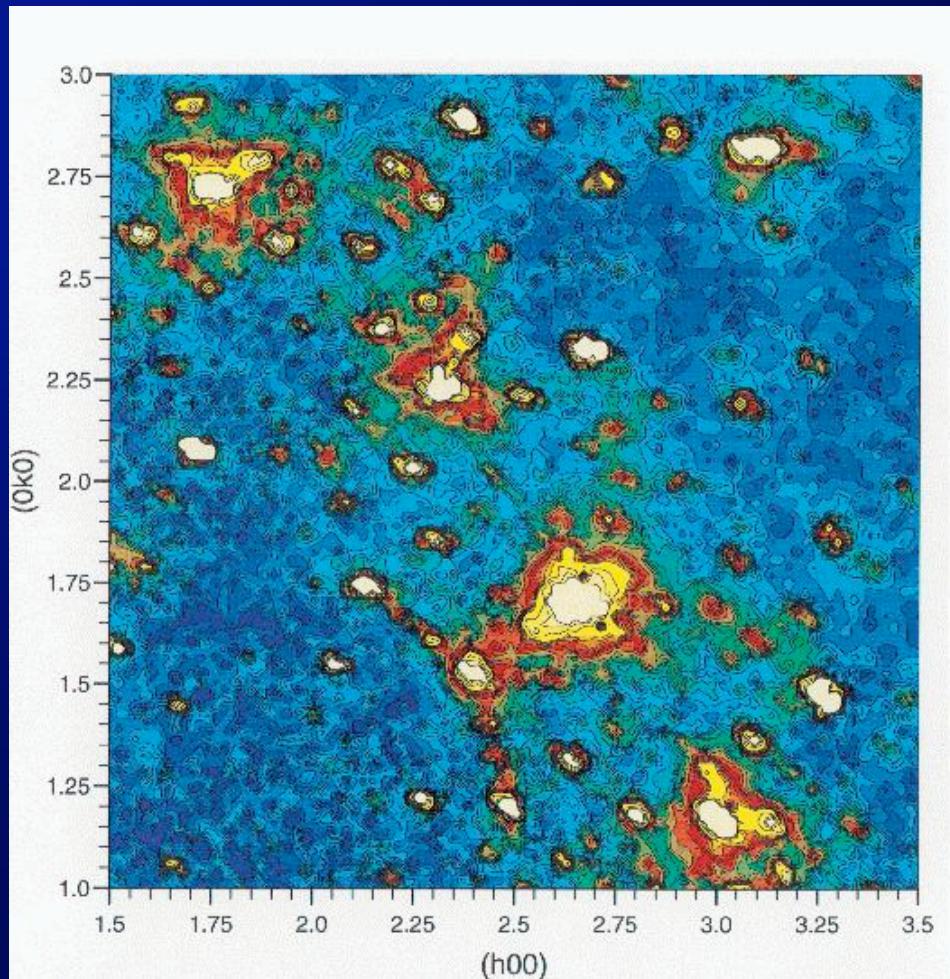
ISIS SXD

$\text{Al}_{71}\text{Ni}_{16}\text{Co}_{13}$ (QX39)

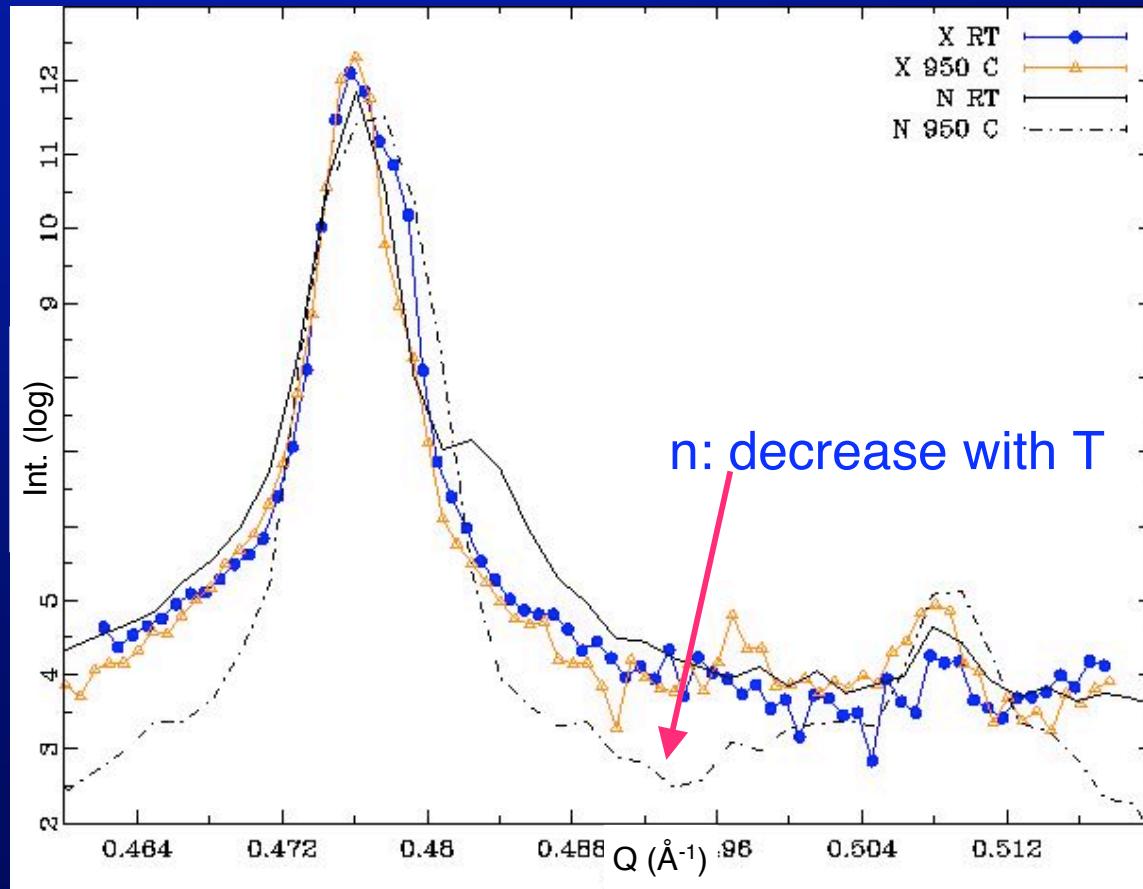
T=30K

$h_1 h_2 h_3 h_4 0$ -layer

Maximum Q-value
corresponds to 2.5\AA^{-1}
compared to $\sim 1\text{\AA}^{-1}$ for
x-rays (0.71\AA)



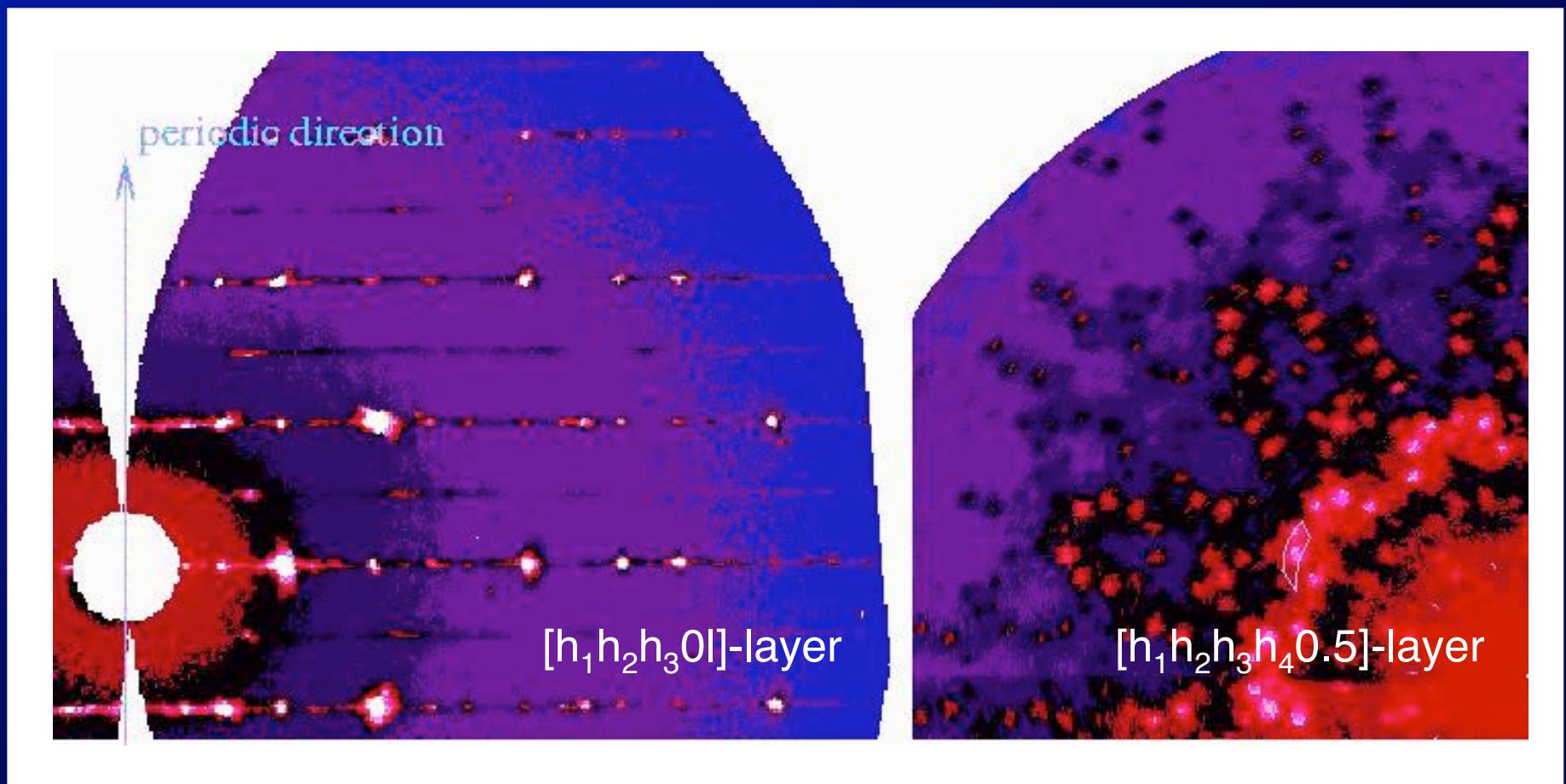
Comparison x-ray and neutron scattering



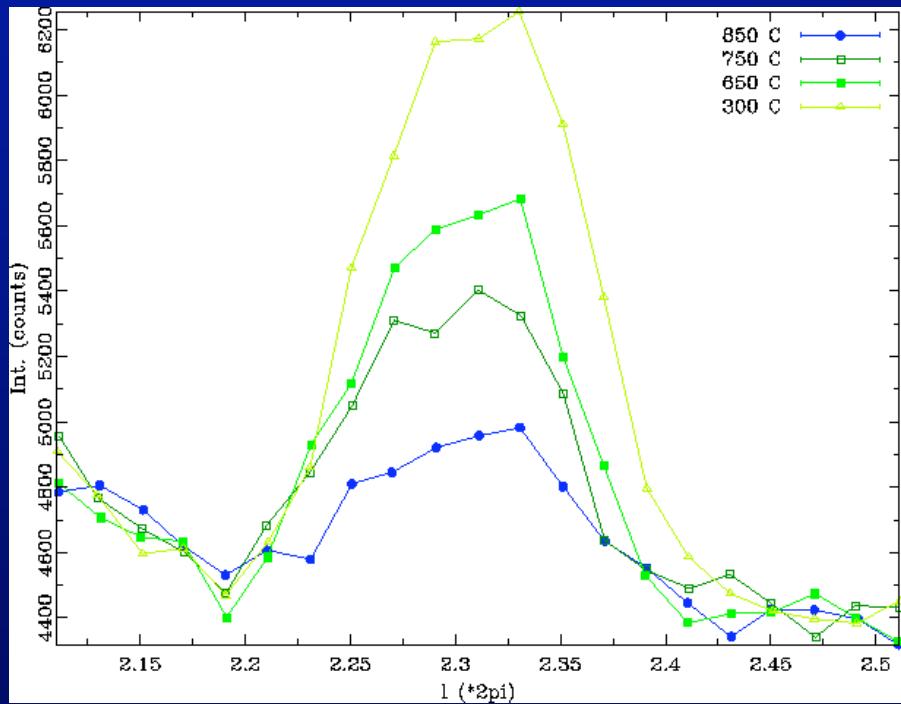
Advantages of neutron methods

- Contrasting of TM atoms
- Suppression of TDS
- sample environment (heating)
- sample size: integration

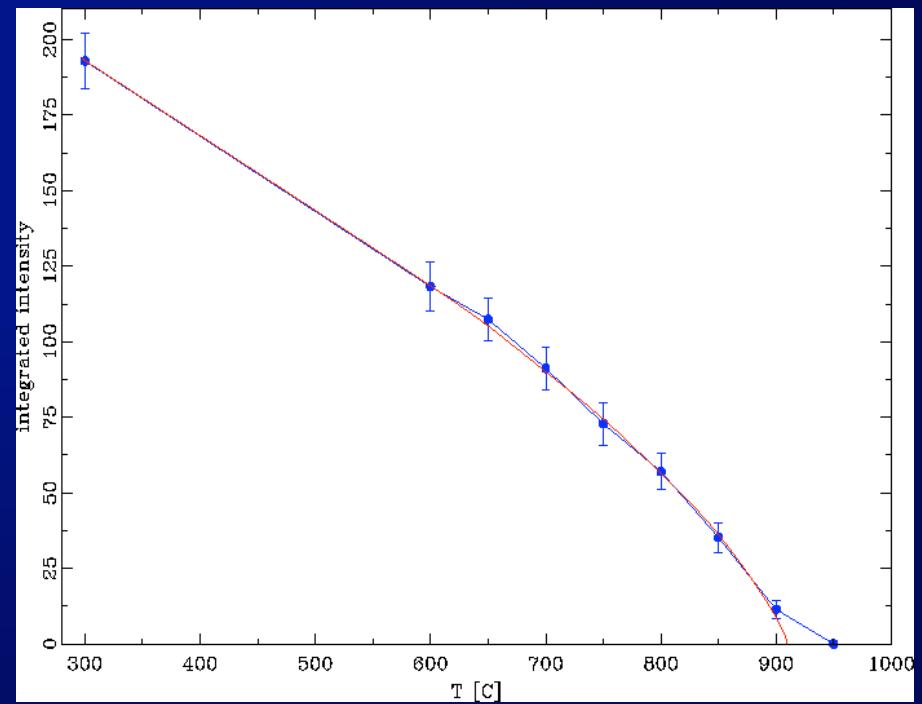
Diffuse layer line system



Temperature dependence of diffuse background $\text{Al}_{72}\text{Co}_{16}\text{Ni}_{12}$

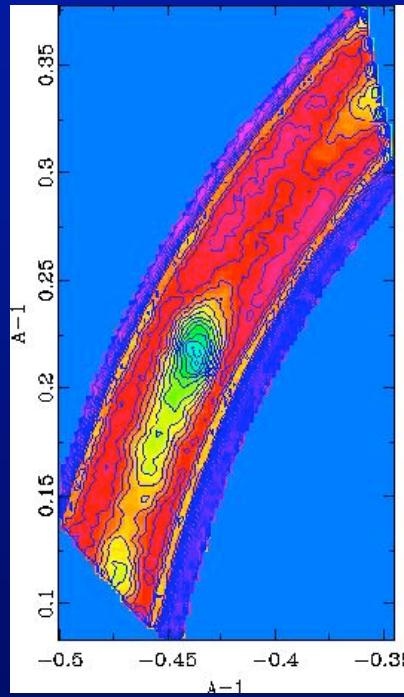


Scans along l , 2nd diffuse layer
 $h=0$, $k=0.4$, IN8/ILL cooling cycle



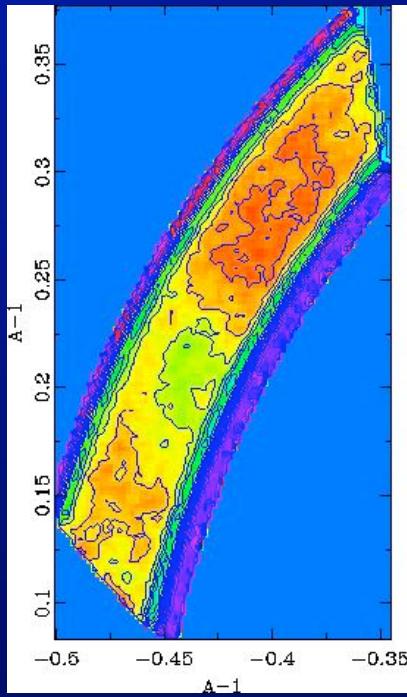
Fitting with power law gives
 $T_c = 911 \pm 3^\circ\text{C}$, $\alpha = 0.36$

Temperature dependence of sro-maxima

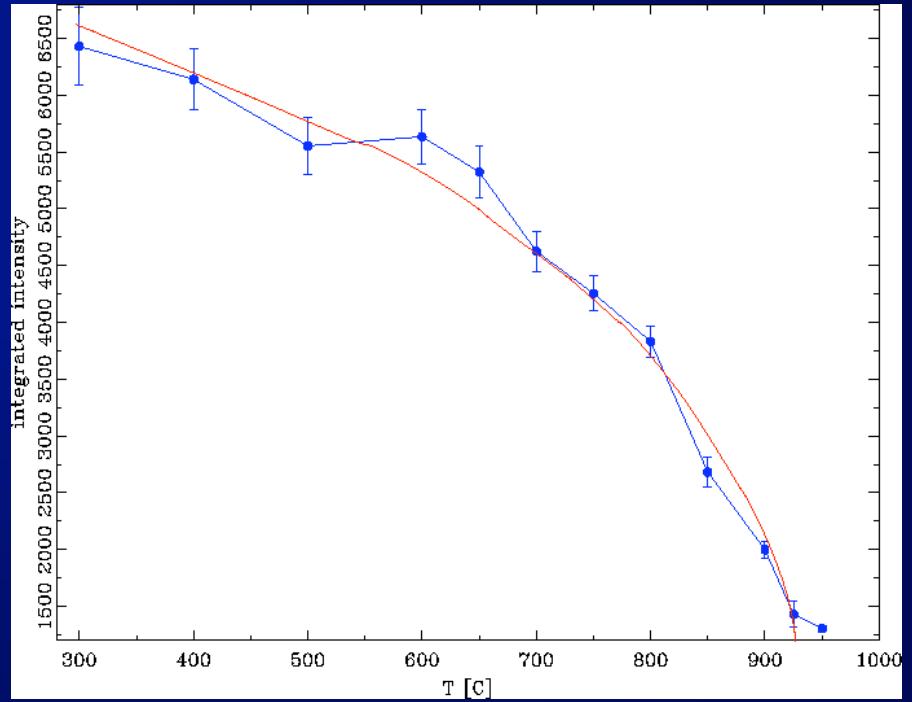


780 °C

Area detector measurement,
1st diffuse layer, D10/ILL



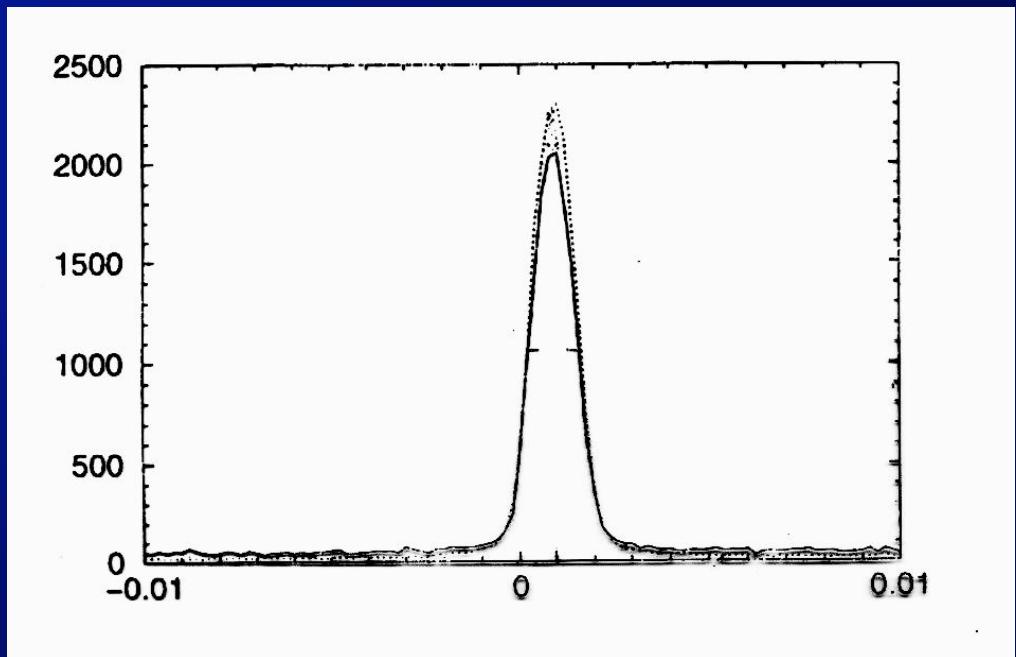
900 °C



Fitting with power law gives
 $T_c = 933 \pm 13$ °C, $\alpha = 0.18$

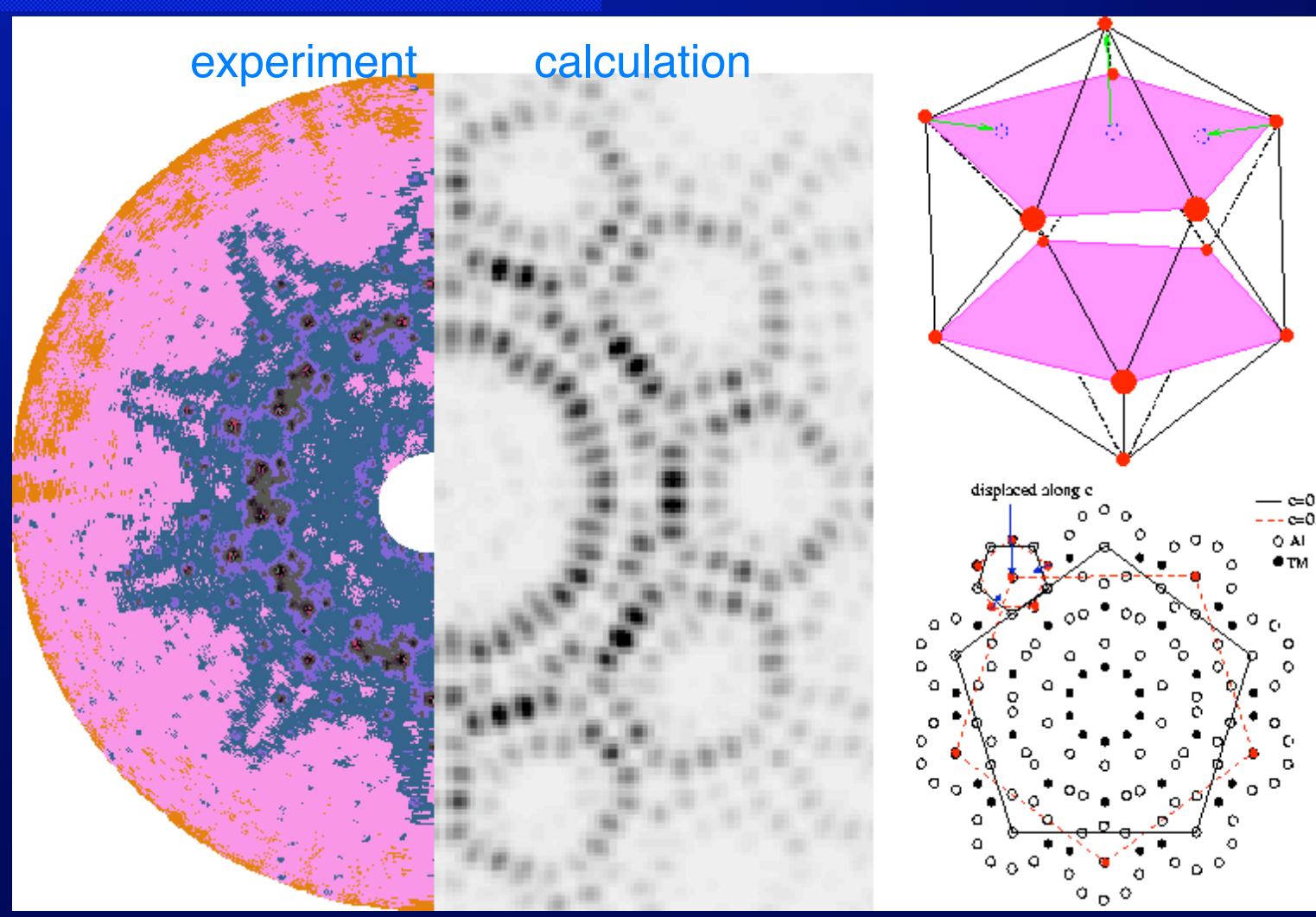
Anomalous Scattering Experiment

decagonal $\text{Al}_{72}\text{Co}_{16}\text{Ni}_{12}$
ESRF/D2AM
close to the Co-K \square edge
(7.7 KeV, 7.4 KeV)
Integrated intensity
 \square 10% change (after
corrections)



scan through the diffuse background
at l=0 position, small Q

Modulation of diffuse layers: computer simulation



columnar
cluster model

structure
model

Final remark - Software

Data recording (against time or monitor-rate), data storage

- single detector, optimum scanning, resolution considerations
- Area detectors

dynamic range

efficiency calibration (IP, CCD, multidetector)

(□ storage of raw data)

background subtraction from diffuse signals (not trivial!)

(□ neutrons IP's?)

□/n- contamination?

Final remark - Software

Data transfer into 'undistorted' reciprocal (Q-) space

- transformation of coordinates
- geometrical corrections
- weighting of pixels
- sections, integrations

- X-ray case: absorption correction

Data analysis

- qualitatively (models)
- quantitatively: resolution corrections, statistical descriptors?

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(CNRS)

R. Neder (*)

T. Proffen (*)

T. Scholpp (*)

E. Weidner

....and collaborators

C. Paulmann, H.-G. Krane (DESY)

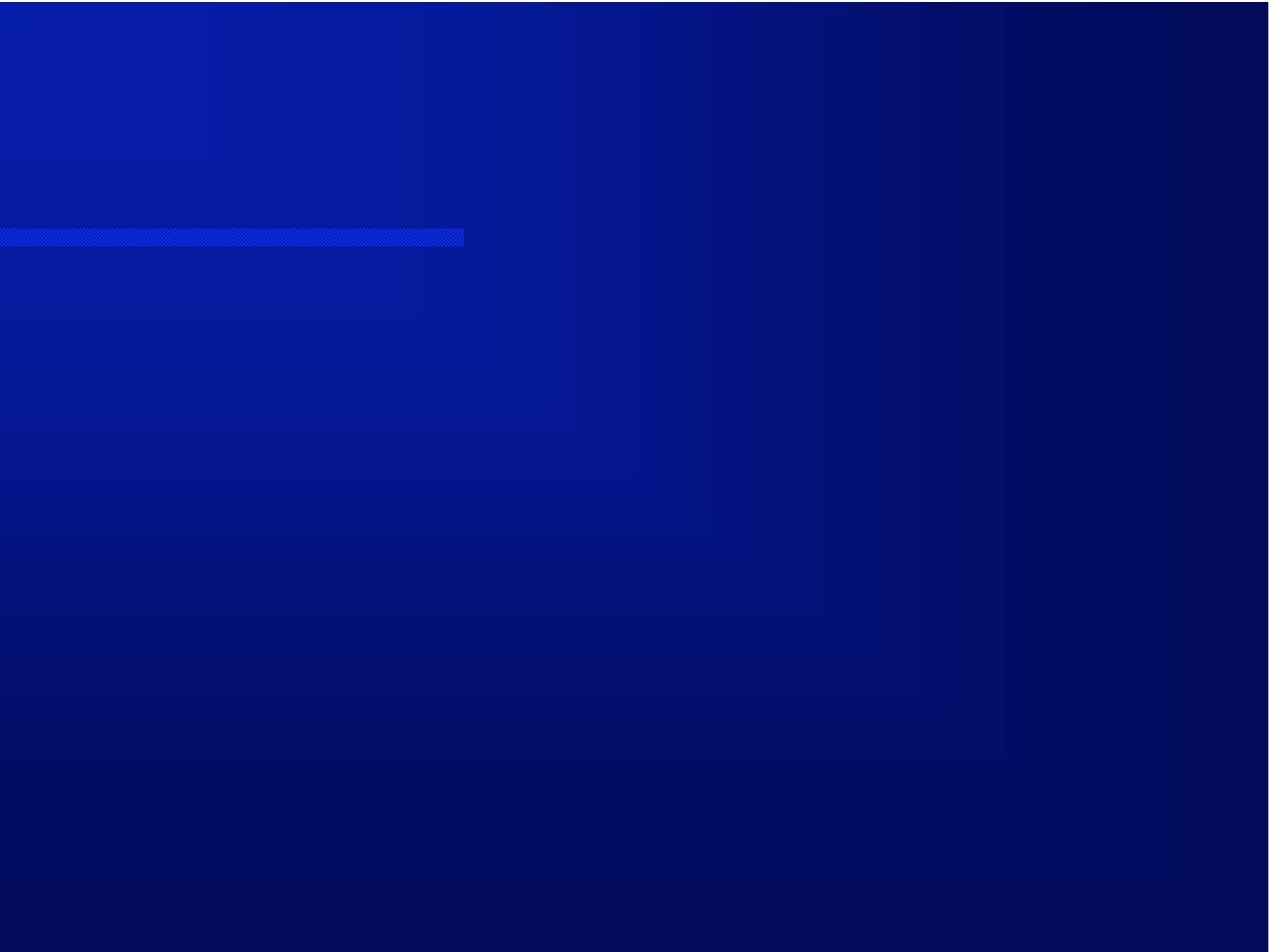
J. U. Hoffmann (BENSC/HMI)

D. Keen (ISIS/RAL)

M. deBoissieu, A. Letoublon

A. Mazuelas (ESRF)

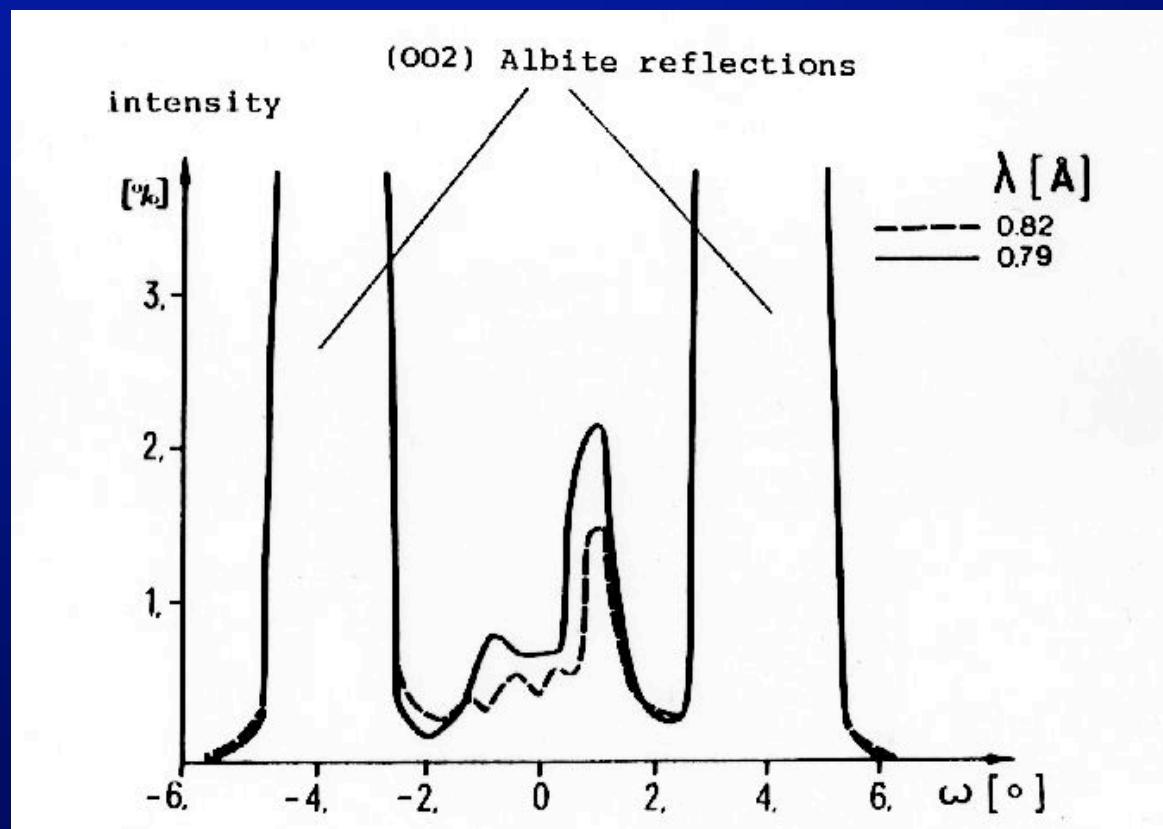
G. McIntyre, R. Currat (ILL)



Albite twin reflections and connecting streak

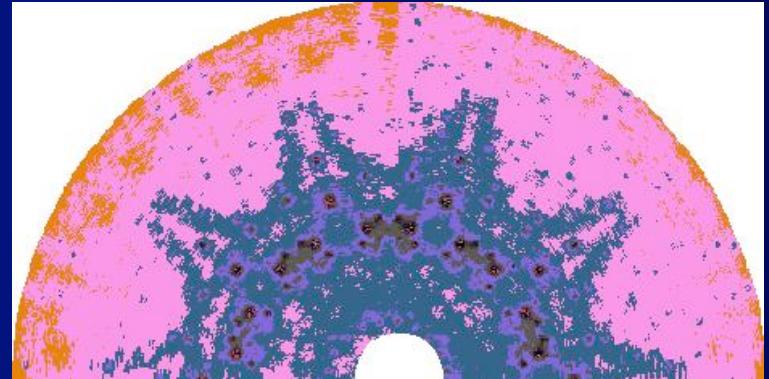


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Jagodzinski et al.

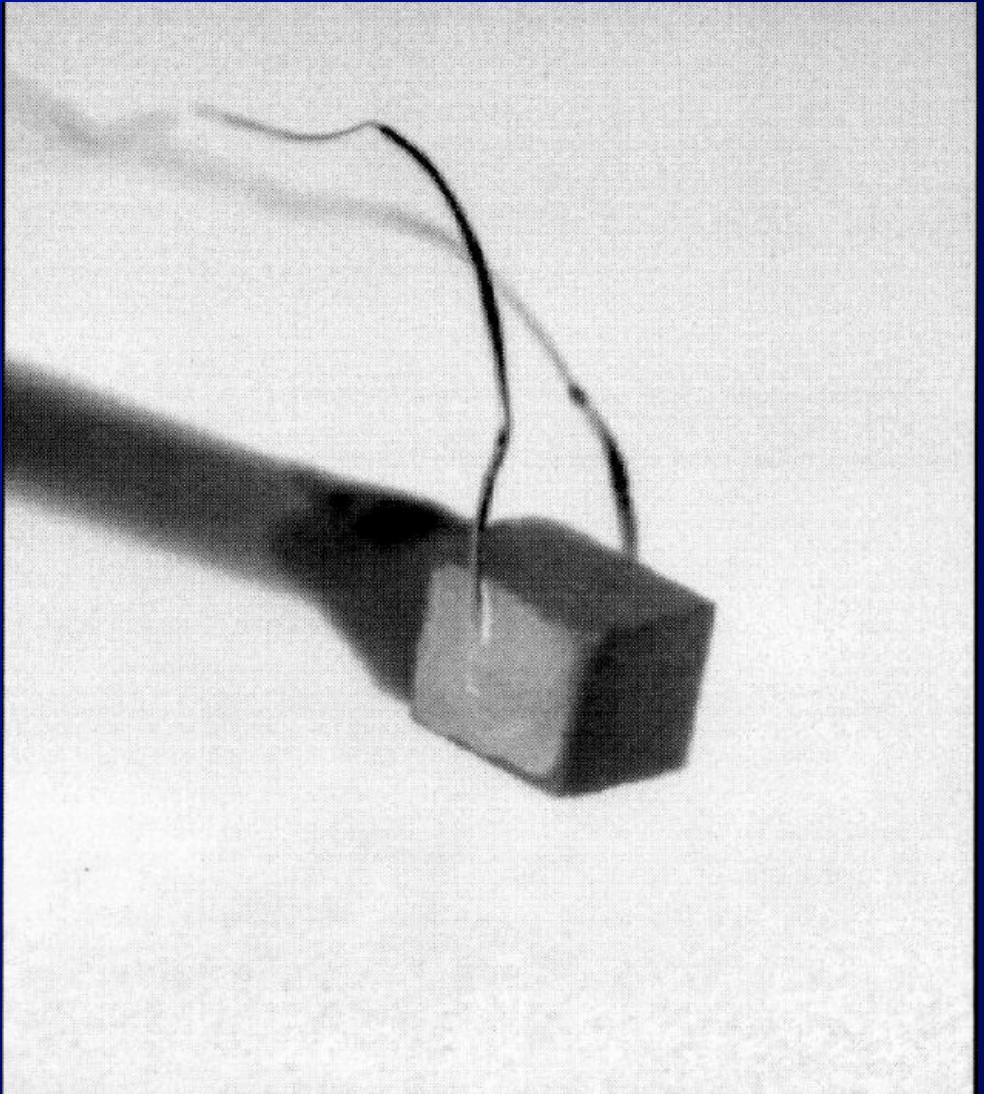
Origin of disorder in crystals and quasicrystals



- coordination problems in a structure
- cooperative precursors of phase transformations (e.g. melting)
- final stages of irreversible processes – phase transitions (kinetics)
- electronics (Hume-Rothery mechanism)
- strain release (strain energy)
- intergrowth (coherent/incoherent)
- entropy (qc-phases)

Applied electric field

YSZ single crystal,
15 mole% Y_2O_3
porous Pt electrodes



Fwhm of diffuse maxima vs. electric field

Zirconia CSZ (15mol%CaO) – 1000K

